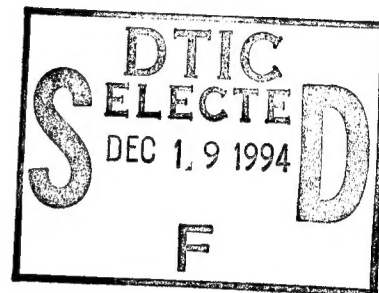


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**LATTICE PARAMETERS AND
DEBYE-WALLER FACTORS
OF γ -TiAl ALLOYS**

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ABSTRACT

Accurate lattice parameters of the tetragonal γ TiAl phase with the L10 structure have been determined by X-ray diffraction. The results showed that in binary alloys, the 'a' parameter decreases while the 'c' parameter increases with increasing Al content. Integrated X-ray intensity were determined from annealed powder samples with powder size $< 5\mu\text{m}$ in order to estimate the temperature factors. Difficulties associated with such evaluations due to the effects of extinction are also discussed. In addition, the 110, 111, and 200 structure factor amplitudes of γ phase Ti-56 at. % Al alloy were accurately determined from critical-voltage electron diffraction measurements. The Debye-Waller factors determined from X-ray experiments and the critical voltage experiments are compared and the results discussed.

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INTRODUCTION

The γ -TiAl phase which possesses many attractive properties such as low density and high temperature strength is primarily limited in its use as a high temperature structural material due to its brittleness at room temperature. Consequently, substantial research efforts are devoted to the improvement of its ductility. In particular, the effect of stoichiometry, ternary additions and novel alloying and fabrication techniques on the stability and mechanical properties of the γ -TiAl phase are being explored. Fundamental to the understanding of the consequences of these studies is a knowledge of the interatomic bonding characteristics of binary alloys. Subsequently, a thorough investigation of bonding mechanisms upon ternary additions to the γ -TiAl phase which would cause a rearrangement of the valence electron distribution is extremely important. A clear understanding of the bonding mechanisms by examination of the electron charge densities is expected to provide a better guidance to providing a solution to the brittleness problem in intermetallic alloys.

Accurate atomic structure factor measurements are a prerequisite to determining electron charge distributions. The charge distribution and the structure factors depend on the vibration of the atoms about their mean atomic positions and hence accurate knowledge of the precise lattice constants and the temperature factors are key parameters essential to the solution of the entire problem. Accurate lattice constants and temperature factor (or the x-ray Debye-Waller factor) for a Ti-51 at. % Al alloy have recently been reported [1]. The only accurate determination for the variation of lattice constants of the γ -TiAl phase as a function of alloy composition was carried out by Duwez and Taylor in 1952 [2]. Though several reports on lattice constants of binary [3-6] as well as ternary [7] and rapidly solidified metastable γ phase as a function of alloying contents [8] are available, no systematic work aimed at precise lattice constants have been made so far. Hence, in this work, attention was initially paid to fill in this lacuna in research on γ -TiAl phase alloys. Subsequently, Debye-Waller factors and low angle structure factors were also determined.

EXPERIMENTAL PROCEDURE

As cast ingots of Ti-Al alloys were prepared either Materials Laboratory, Wright-Patterson Airforce Base, Dayton or at NAWC. The alloys were homogenized, turnings made on a lathe and then pulverized using a pestle and mortar. The powders were initially passed through a 400 mesh (38 micrometer) sieve. These powders were further ground and sieved through electrically formed metallic mesh screens of 20, 10 and finally 5 micrometers spacing. The

experiment was carried out using a special acoustic sieving device. Details of the procedure can be found in Ref. 2.

RESULTS AND DISCUSSION

Precise determination of lattice parameters

Precise lattice parameters of γ -TiAl phase were determined as a function of Al concentration. We have obtained x-ray data from annealed alloys as well as annealed powder samples of the same alloys. X-ray diffraction data from all the samples showed 30-50 sharp lines (including several well resolved K_{α_1} and K_{α_2} reflections) arising from both fundamental and superlattice reflections. The X-ray data were analyzed by the mathematical procedure suggested by Vogel and Kempter [9] that incorporates a weighted linear least square method of computation. The standard deviations in the lattice parameters obtained from such an analysis were found to be between 3×10^{-6} and 3×10^{-5} . The error in the data expressed as $\left(\frac{\sin^2 \theta_{\text{observed}} - \sin^2 \theta_{\text{calculated}}}{\sin^2 \theta_{\text{calculated}}} \right)$ was always found to be within $\pm 1\%$ or less as seen from the examples in Figure 1. The values of c and a determined in this manner has been plotted in Figure 2 and the results are compared with previous lattice parameters determinations reported in literature. Several observations can be made from this plot :-

(a) The results of the present work indicate that the lattice constants obtained from bulk samples as well as powder samples are almost identical. Typically, the homogenized alloys used in the present study contained ~ 700 ppm of oxygen. This implies that little or no oxygen has been introduced during the powder preparation process or that the γ -TiAl phase has no solubility for oxygen.

(b) The results of the present work and those of Duwez and Taylor [1] are similar though the 'a' parameters found in the present work are smaller and the 'c' parameters are higher. A re-analysis of the lattice constants of the Ti-55at. % Al alloy from the values of θ tabulated in the paper by Duwez and Taylor [2] by using our computer program (weighted least square fit) gave the following results, ' $c = 4.0786$; $a = 3.9847$ '. This value of 'c' is very close to our data though the 'a' is somewhat smaller. It is then clear that the computational technique employed is responsible for some of the differences in the results of different workers. This observation is reiterated by the fact that the results on Ti-50 at. % Al reported by Myers and Davies [5], who employed a graphical solution of data from seven observed lines to compute the lattice constants, and our

data agree very closely. The graphical technique weighs the high angle lines more and thus is quite similar to the method adopted here. However, the computational technique employed in the present work weighs the data in a systematic fashion and is certainly preferred over the graphical method where the researcher makes a judicious choice of the weights.

(c) The addition of Al does not affect the 'c' parameter very much while the 'a' parameter decreases. The trend in the data is in agreement with the results of Duwez and Taylor [1]. The dependence of 'a' on at. % Al observed in the two studies are similar (0.00162 vs 0.00122 in Duwez & Taylor) while the rate of increase of 'c' with composition reported by Duwez and Taylor [1] (0.00075) is five times larger.

(d) The results of other workers presumably contain more experimental as well as computational inaccuracies and cannot be compared here. It must be remembered that the two earliest reports (Ogden et al. [4] and Bumps et al. [3]) are reports on the equilibrium phases, crystal structure and phase diagram of Ti-Al alloys and the x-ray data may not have been aimed at reporting accurate lattice constants.

(e) Based on these discussions, it is clear that the present work reports the most accurate lattice constants of the γ -TiAl phase.

Temperature factors of γ -TiAl phase Alloys

The x-ray intensity of a Bragg reflection, I_{hkl} is expressed as:

$$I_{hkl} = K |F|^2 p \phi(\theta) \exp^{-2M} \quad (1)$$

where K is a constant related to the diffractometer, F is the structure factor, p is the multiplicity factor, θ is the Bragg angle, $\phi(\theta)$ is the Lorentz - Polarization factor and M is the temperature factor. The temperature factor M is related to the Debye-Waller factor, B, through :

$$M = B \frac{\sin^2 \theta}{\lambda^2} \quad (2)$$

where λ is the wavelength of the x-rays. In equation (1), F, p and $\phi(\theta)$ can be calculated and combining equations (1) and (2) we get,

$$I_{hkl} = K' \exp^{-2B \frac{\sin^2 \theta}{\lambda^2}} \quad (3)$$

where

$$K' = K |F|^2 p \phi(\theta)$$

The Debye-Waller factor, B may then be determined from a measurement of the x-ray integrated intensity of a reflection (hkl) and the use of equation (3) i.e., the slope of the plot of $(\ln I_{hkl})$ vs $\frac{\sin^2 \theta}{\lambda^2}$. Such a plot is known as Wilson plot. Accurate determination of I_{hkl} is difficult since the experiment requires strain-free, extinction free powders. By using well annealed fine powders having a size < 5 micrometers, Fox et al. [2] showed that accurate x-ray intensity measurements can indeed be made. The powders were produced by mechanical methods and an acoustic sieve was used to separate sub 5 micrometer particles. An example of a Wilson plot from a Ti-56at. % Al alloy is shown in Figure 3 by the square symbols. In the calculation for the intensity, I_{hkl} , the values of the atomic scattering factors are required. The free atom scattering factors calculated by Doyle and Turner [10] were used in this calculation. The data does not lie on a straight line as expected from equation (3). Note that the intensity of the high angle reflections fall on a straight line while the intensity of the lower angle reflections are much less than that expected. The nature of the data, i.e., the lower intensities at low Bragg angles suggest that these reflections suffer extinction. This implies that even when the particle size has been reduced to < 5 mm, significant extinction occurs especially in the fundamental (110) and (111) reflections. In order to examine this hypothesis, the nature of extinction in TiAl was calculated using the theory developed by Sabine [11]. Figure 4 shows the extinction factor for the several reflections in TiAl as a function of the grain size. Here the extinction factor, E, is defined as:

$$E = \frac{\text{Integrated Intensity}}{\text{Kinematical Intensity}}$$

It is clear from Figure 4 that extinction is significant and should be corrected for when determining the integrated intensities in TiAl. Accordingly, the x-ray integrated intensity data shown as squares in Figure 3 were corrected for extinction and the corrected intensities are shown as open circles in Figure 3. The data clearly falls on a straight line and Debye - Waller factor was determined from the slope of the line to be 0.760 for Ti-56 at. % Al. Similar

experiments for Ti-50 at. % Al have been performed earlier by Fox, Stoner and Cade [2] and their x-ray data was corrected for extinction and the Debye-Waller factor determined. Figure 5 shows the plot of the Debye-Waller factor as a function of at. % Al. There is a significant increase in the Debye-Waller factor of the γ -TiAl phase with increasing Al. Experimental work on binary γ -Ti-54at. % Al alloy has just been completed and the data is being analyzed.

Critical Voltage Measurements in γ -TiAl Alloys

Electron diffraction measurements of the x-ray structure factors of stoichiometric γ -TiAl and γ -Ti - 56 at. % Al have also been made using the 1.5 MeV high voltage electron microscope (HVEM) at the National Center for Electron Microscopy (NCEM), Lawrence Berkeley Laboratory, University of California. Details of the theory involved in such measurements can be found in references 12-15. The work on the Ti - 56at. % Al alloy is still in progress. Table 1 shows the results on the critical voltages for several reflections of the two alloys obtained so far. In the stoichiometric alloy, from the HVEM measurements, the Debye-Waller factor and charge density have been determined (Fox [15] and Lu, Zunger and Fox [16]). The Debye-Waller factors determined from the critical voltage measurements are also included in Table 1. The results in Table 1 on measurements on the Ti-56at. % Al alloy indicate that the structure factor changes associated with adding Al to stoichiometric γ -TiAl alloy are associated with changes in lattice parameter, increase in Al content, static displacements due to Al antistructure defects and charge transfer effects due to solid solution alloying. These results are currently being analyzed to obtain charge density distributions in off-stoichiometric γ -TiAl phase alloys.

Systematic row	Reflection minimizing	Critical Voltage in kV	
		Ti-50at. % Al	Ti-56at. % Al
001	004	738 \pm 10	
001	005	1310 \pm 40	
110	330	317 \pm 10	~300
111	222	329 \pm 3 at 298 K	321 \pm 4
111	222	285 \pm 5 at 699 K	
200	400	732 \pm 10	724.5 \pm 7.5
200	400	605 \pm 15 at 702 K	~590 \pm 10 at 688 K
201	603	1250 \pm 100	
112	336	>1450	
Debye - Waller factor		0.47 \AA^2	0.62 \AA^2

The Debye-Waller factors determined from the x-ray experiments and those obtained from the HVEM measurements are shown in Figure 5, showing a clear disparity in the results. Also shown on this plot is the Debye-Waller factor determined by Swaminathan et al. [17] for the Ti-52at. % Al alloy, $B = 0.67 \text{ \AA}^2$, which is in good agreement with our x-ray results. However, it must be cautioned that the values of structure factor shown in Table 2 (column 4) of the Swaminathan et al. [17] paper is incorrect. Thus, though the Debye-Waller factor appears to be consistent with our data, the value of B reported too must be deemed incorrect.

The origin of the difference between the Debye-Waller factors determined by x-ray diffraction and critical voltage measurement by means of the HVEM arises from the fact that, when computing the expected intensity of x-ray reflections, the free atom scattering factors calculated by Doyle and Turner [10] were used while the Debye-Waller factors determined from the HVEM data uses the experimentally determined structure factors of TiAl. In order to test this hypothesis, The Debye-Waller factor of the stoichiometric TiAl alloy was recalculated using the recently reported [16] first principle local density calculations of the structure factors of TiAl. This data is shown in Figure 6 and it can be seen that the x-ray Debye-Waller factor determined for TiAl ($B = 0.45 \text{ \AA}^2$) is very close to that determined by HVEM experiments. ($B = 0.47 \text{ \AA}^2$). Similar calculations for the off-stoichiometric alloys are not possible since accurate theoretical structure factors for several high angle reflections are not available. However, it is clear that the use of structure factors of TiAl calculated using free atom models are not satisfactory for the analysis of x-ray diffraction data, even for high angle reflections.

Work on more binary and some ternary alloys is currently in progress.

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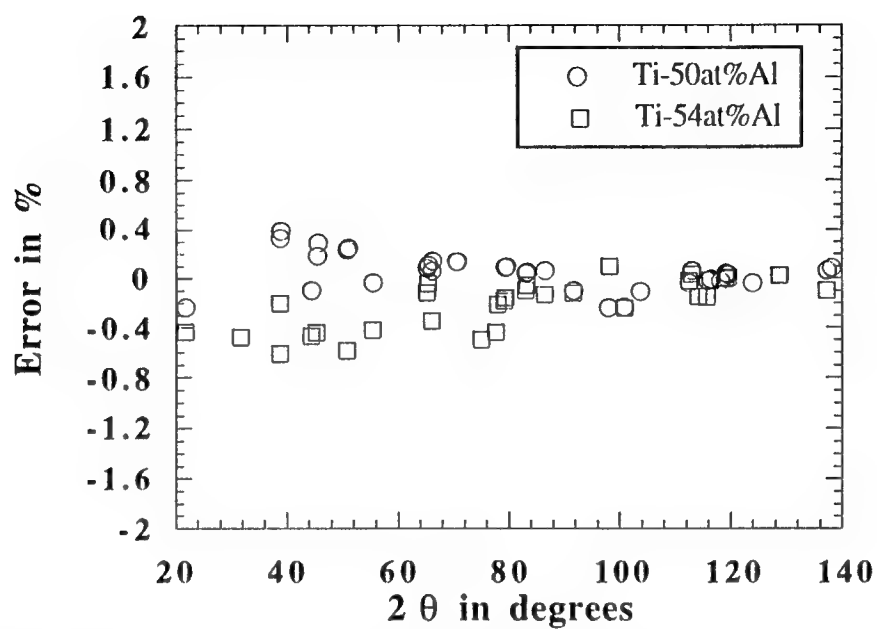
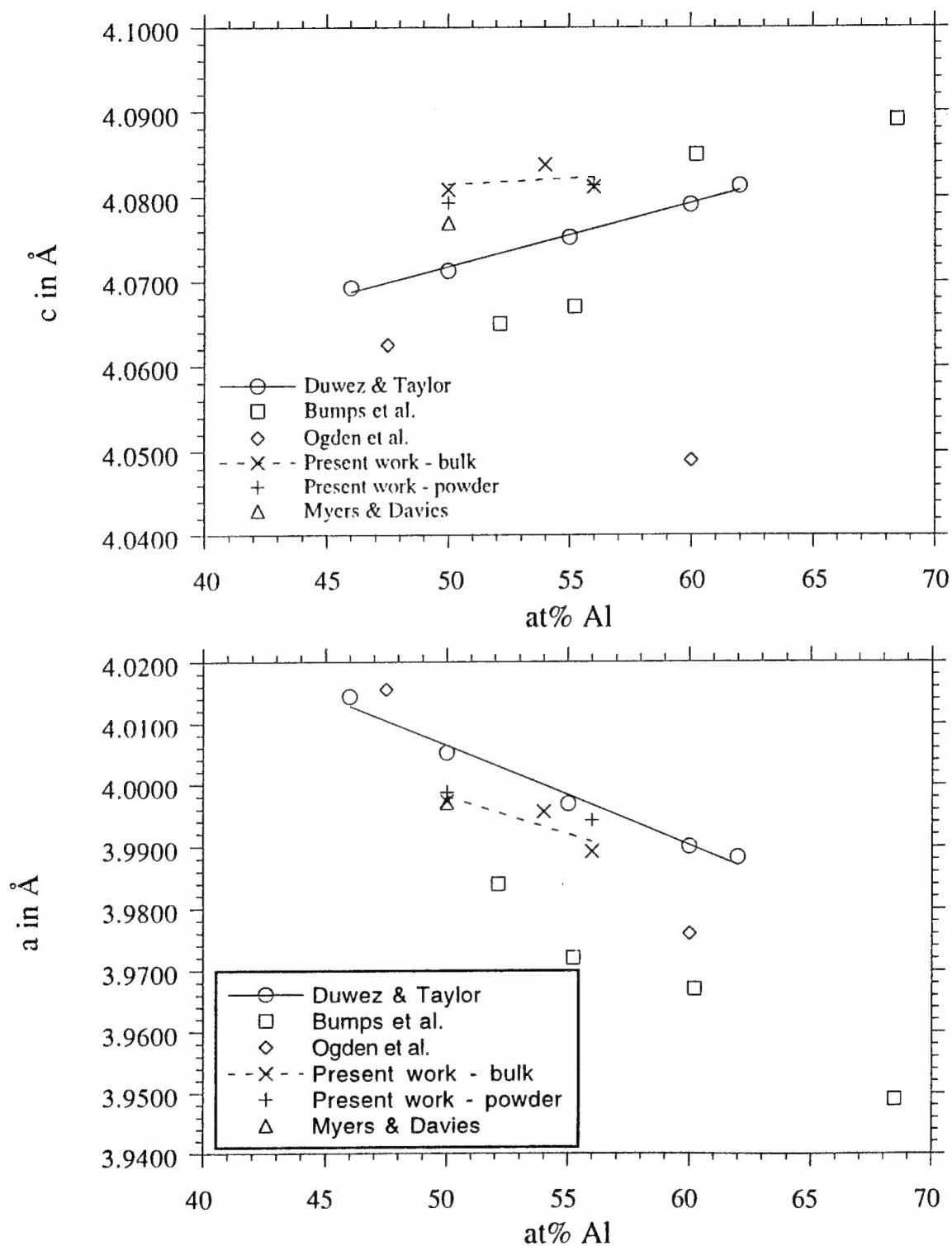


FIGURE 1: Error in the calculated values of $\sin^2\theta$ as a function of 2θ .



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FIGURE 2 : Lattice constants of TiAl as a function of composition.

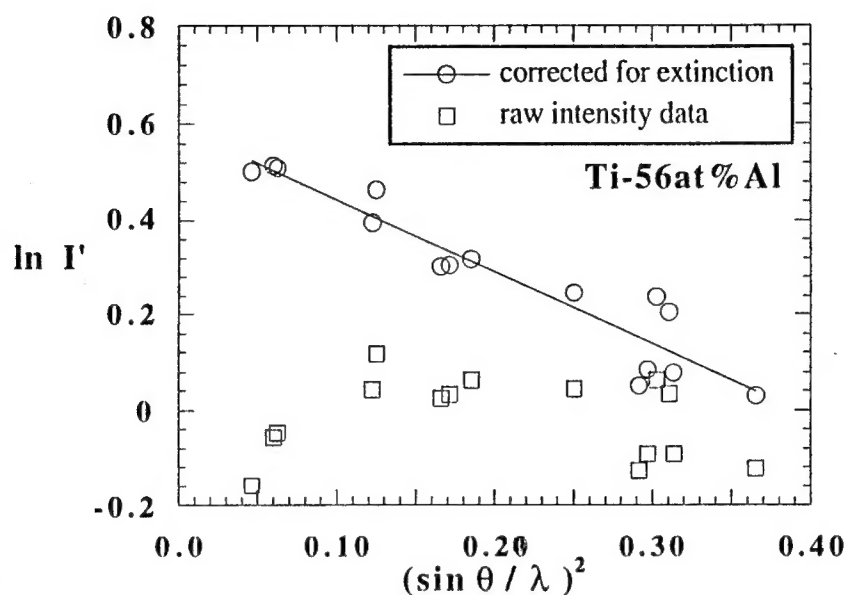


FIGURE 3: Wilson plot for Ti-56at. % Al. The Debye-Waller factor B , calculated from the data (open circles) is $B = 0.76 \pm 0.035 \text{ \AA}^2$.

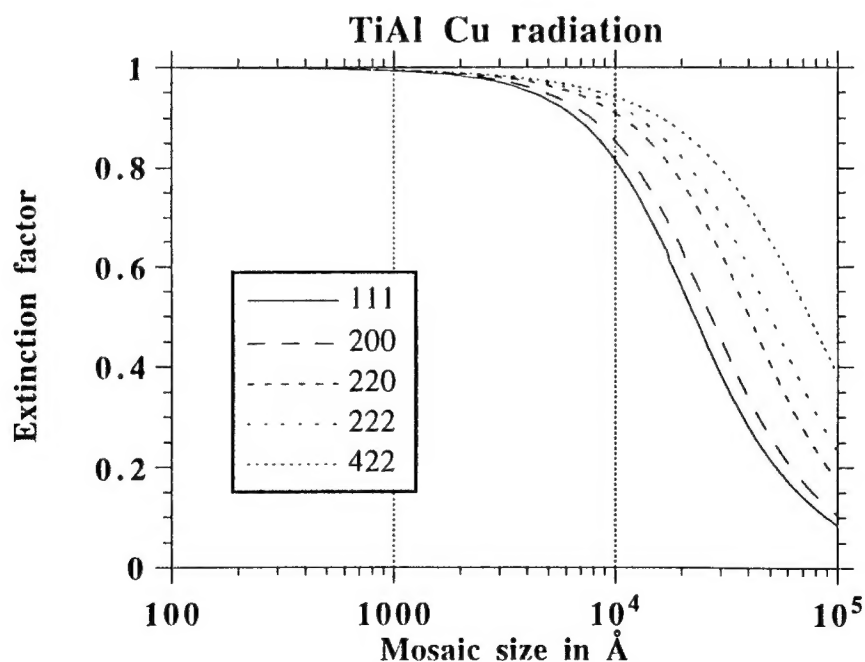


FIGURE 4 : Extinction factors in Ti50at. % Al for Cu K_{α} as a function of grain size.

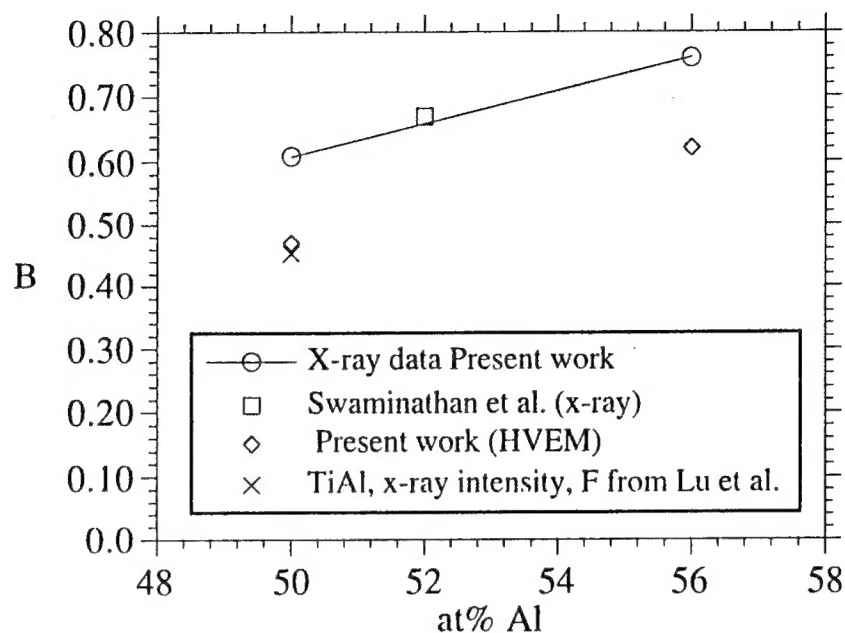


FIGURE 5 : Debye-Waller factors of TiAl alloys

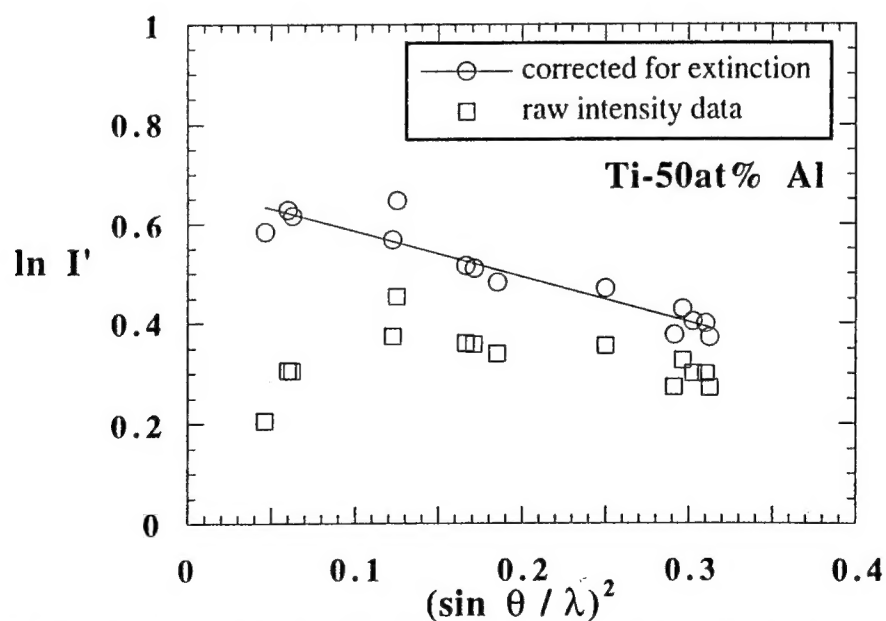


FIGURE 6 : Wilson plot for Ti-50at. % Al. The atomic scattering factors calculated in Ref. 16 are used in the calculations here. $B = 0.453 \pm 0.025 \text{ \AA}^2$.

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